8 Forces between atoms

In our everyday dealings with matter, the 'isolated atom' is rare and is encountered considerably less frequently than are *molecules* - i.e. a collection of *aggregated atoms*. For example, all of our bodily experiences including, breathing air, digesting food, and the formation of DNA in the cell include chemical reactions that involve taking apart one molecule and recombining its constituent atoms to form other molecules. Our very existence is as inextricably linked to the nature of molecules as it is to that of atoms or nuclei. Molecules are by no means restricted to our local environment. Astronomical observations have shown that 'molecular clouds' are spread throughout the universe and some molecules that do not occur naturally on Earth have been discovered in space [e.g. Argon hydride (ArH) was recently discovered in the Crab Nebula - the remains of a star that exploded 1000 years ago]. It would therefore seem that molecules may be equally fundamental to our understanding of nature on every scale from the cosmological to the biological. It is fitting therefore, that we consider the forces that hold molecules together and the types of *bonding* that results

8.1 Types of bond

- **Ionic bond** (e.g. NaCl): Atom 1 (Na) loses electron to atom 2 (Cl)

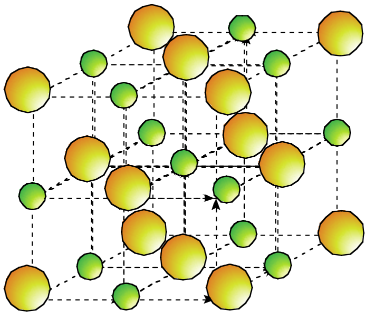

Figure 28: Ionic crystal

Hydrogen along with the group I alkali metals (Li, Na, Rb, Cs) all have a single electron in their outer shell. When one of these react with anyone of the group VII halogens (F, Cl, Br, I) which are one electron short of completing an outer shell, they form *ionic bonds*. Typical bonding occurs between metals (which liberate electrons easily through *ionisation*) and those non-metals which have a strong *electron affinity* which is a measure of the ability of an atom to attract an electron. It is most significant for elements in groups 6 and 7 of the periodic table and increases as the number of electrons required to complete the outer electron shell decreases.
Thus, the attractive force between +ve & -ve ions are governed by Coulomb's force $F \propto q_1 q_2 / r^2$ so that $U \propto V_r \propto 1/r$.
When **ionic crystals** (crystals of monatomic ions such as NaCl) are modelled by stacks of hard spheres it is essential to allow for the different ionic radii (typically cations are smaller than anions) and different charges (fig. 28). This normally limits the packing and renders

Note one ion can bond to many near neighbours - as many as packing will allow.

ionic crystals in the main less dense than metals. The **coordination number** of an ion is the number of nearest neighbours of opposite charge. For ionic crystals a maximum coordination number of 8 is exhibited by Cs; whilst for most other ions it is less than this (usually 6 or less).

- **Covalent bond** (e.g. C in diamond):

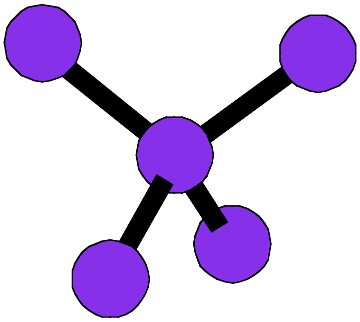

Figure 29: Covalent bonds

Covalent bonds occur between non-metallic elements in the periodic table. An electron pair is *shared* between neighbouring atoms to form usually saturated, and normally short-scale structures (i.e. molecules). They are also responsible for some strong giant structures however (e.g. diamond). Briefly, one or more electron from each atom is donated to form a -ve region between the atoms (the bond); the resulting electron cloud then becomes distorted and highly directional (fig. 29.
In reality not all bonds can easily be classified as strictly ionic or covalent. For example, *homonuclear diatomic* molecules (those made up of like nuclei, such as H_2) do not form ionic bonds as they do not form permanent ions within the molecule. However, *hetreronuclear* molecules (those made up of unlike nuclei, i.e. HF) *do* have permanent charge separations (dipoles) and the extent of this separation will determine how ionic or covalent the bond is. E.g. if the lithium electron in LiF spends all of it's time in the vicinity of the fluorine atom, the bond would be considered ionic. Experimental determination of the *electric dipole moment* suggests that lithium's electron does maintain some probability of being on its home base in addition to spending time at fluorine; indicating that this bond is in fact partly ionic *and* partly covalent

- **Metallic bonding**:

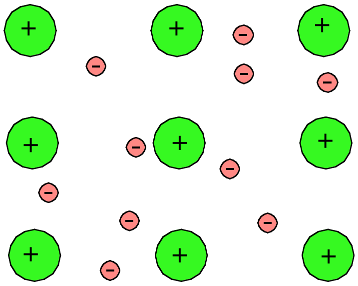

Figure 30: A Metal

As mentioned earlier, metals generally have a low ionisation energy and will liberate their outer electrons easily. It is not surprising therefore that in a metallic crystal structure, electrons can easily dissociate from the atoms to form a 'sea' of electrons (called conduction electrons) which also acts to reduce the repulsion between the (+ve) metal ions. Conduction electrons are said to be *delocalized* because they do not have a specific location (are not localized), rather, they exist in orbitals that include several atoms and/or bonds (fig 30). Many physical properties of metals, such as strength, malleability, ductility, thermal and electrical conductivity, opacity, and luster can be traced back to metallic bonding.

- **Van der Waal's forces** :

Atoms of the noble gases have closed electronic shells and do not interact with one another via covalent or ionic forces. There is however a weak attraction between such atoms however called the *Van der Waals force*. This force is also present between molecules which in the case of polar molecules, can also interact via fixed dipole interactions. The Van der Waals attractive force is responsible for the condensation of Helium at low temperatures, for example. The attraction arises from the fact that an electron cloud is not totally symmetric at any one time and as such, a local charge separation occurs, causing an **induced dipole-dipole** effect between neighbouring atoms. Suppose two neutral Ar atoms approach one another, on one atom the electron and the nucleus that it is orbiting form a dipole. This fluctuating dipole creates an electric field $\mathbf{E}_d$, that is felt by a second (otherwise neutral) atom whose positive charge is pulled one way and negative the other, that is it becomes *polarised* (see fig. 31). This process does not have to be restricted to two atoms or molecules. If the separation distance is small then synchronised movement of electrons can occur over large numbers of atoms or molecules to form lattices held together by Van der Waals forces.

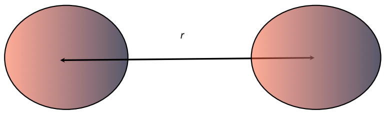

Figure 31: fluctuating → e cloud not symmetric → dipole E

Attractive force: It can be shown that the attractive potential energy due to induced dipoles on neutral atoms (and molecules) scales with distance as $\frac{1}{r^6}$. The interaction is known as the London interaction after Fritz London who first described it. The London interaction provides the mechanism for the van der Waals force between neutral atoms and will scale as $F_{vdW} \propto -1/r^7$.

Further details of the scaling of the attractive potential energy with distance is given in the Molecular Interactions chapter of the book 'Physical Chemistry' by P.W.Atkins, Oxford University Press (2008).

Repulsive force: Atoms of the noble gases are attracted to one another only by Van der Waals force. When they approach so closely that their electron clouds overlap, the *Pauli principle* causes a repulsive force which dominates the attractive forces and increases rapidly with decreasing internuclear separation. To a first approximation we can usually take $U \propto 1/r^{12}$ [i.e. $(1/r^6)^2$ → simplifying algebra].

In 1925 Lennard-Jones proposed a mathematical form of potential energy, U_{LJ}, that included both attractive and repulsive effects:

$$U_{LJ} = \frac{A}{r^{12}} - \frac{B}{r^6}$$

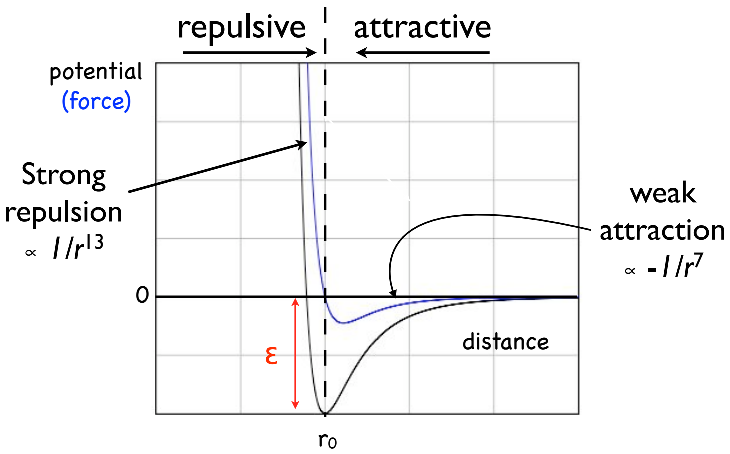

Figure 32: Lennard-Jones 6-12 potential, showing repulsive and attractive regions

where the first term represents repulsions and the second term attractions. We can rewrite the above expression in terms of the equilibrium separation distance, r_0, and binding energy ϵ (see PS3) to give:

$$\boxed{U_{LJ} = \epsilon\left(\frac{r_0}{r}\right)^{12} - 2\epsilon\left(\frac{r_0}{r}\right)^{6}} \tag{15}$$

L-J 6-12 potential

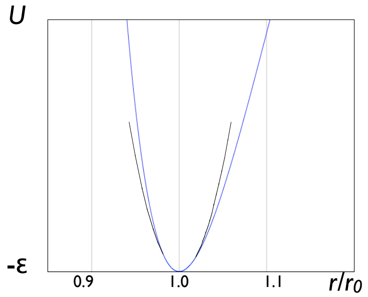

Figure 33: Close up of equilibrium position

The force between two neutral atoms is the derivative of the Lennard-Jones potential (see fig. 32) and we note that the force is positive for $r < r_0$ and negative for $r > r_0$ thereby acting as a *restoring force*. We can go on to show that molecules bound by vdW interaction can be approximated as simple harmonic oscillators - provided the amplitude is small compared to r_0 [see Young & Freedman ch.13 for a fuller treatment].

With the advent of **atomic force microscopy** (lecture 1), it has become possible to measure directly the forces acting between molecules and making comparisons with calculations using (the slope of) the LJ potential. As such there is plenty of evidence to show that $1/r^{12}$ is a fairly poor representation of the repulsive potential and that an exponential form e^{-r/r_0} would be far superior (PS3 invites you to explore why this might be from a conceptual level).

8.2 Vibrations in solids

Consider a particle displaced by δ from equilibrium. Its potential energy increases by $2 \times U_{LJ} = 2 \times \frac{1}{2}k\delta^2$, where $k = \dfrac{d^2U_{LJ}}{dr^2}$.

Hence the particle will vibrate around equilibrium, with a fre-

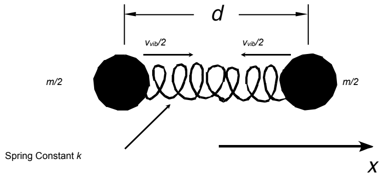

Figure 34: atom vibrates between 2 others

quency given by $\omega_E = \left(144\epsilon/mr_0^2\right)^{1/2}$ (Einstein Frequency). For wavelength $\lambda = r_0$, $v_s =$ speed of sound in solid. These lattice vibrations are often called *phonons* and are quanta of vibrational energy responsible for thermal conduction in solids.

Phonons will be covered extensively in second year courses.

8.3 *Thermal expansion of solids*

Thermal expansion can be thought of as the tendency of matter to change volume in response to a temperature change. Materials generally change their size when subjected to a temperature change while the pressure is held constant. In the special case of solid materials, the pressure does not appreciably affect the size of an object, and so, for solids, it's usually not necessary to specify that the pressure be held constant.

In terms of the interatomic potentials in the solid, as the temperature is raised, the energy and amplitude of vibration also increase (fig. 35). Due to the asymmetric nature of the LJ potential (see fig. 32), we see that as the (total) energy (= pe + ke) of particles in the potential increases, r_0 also increases, hence average bond lengths increase linearly, resulting in $r = r_0(1 + \alpha_L T)$, where α_L is the coefficient of linear expansion. As a result, the change in length of any object to a temperature change ΔT is:

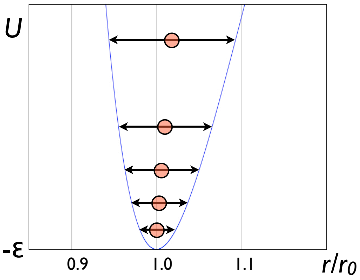

Figure 35: Asymmetry of expansion

The linear increase in average bond length with increasing energy can be shown by performing a third order Taylor expansion on the LJ potential. See Flowers & Mendoza 'Properties of Matter' (1970) p238 onwards.

$$\boxed{\frac{\Delta L}{L_0} = \alpha_L \Delta T}$$

Linear thermal expansion

This equation works well as long as the linear-expansion coefficient does not change much over the change in temperature. If this is not the case, the equation must be integrated. Similarly we can write the volume thermal expansion as:

$$\boxed{\frac{\Delta V}{V_0} = \beta \Delta T}$$

Volume thermal expansion

where β is the volume expansion coefficient. We can also show that for totally isotropic media $\beta \cong 3\alpha_L$ (PS 3).

8.4 *Heat Capacities of solids*

Specific heat capacity is an important property of matter for two reasons. Firstly it has practical consequences in science and engineering because along with thermal conductivity, it determines the thermal interactions that a material has with other objects. Secondly, it is an experimentally measurable quantity that can be compared with theoretical calculations, to test the validity of our model.

In solids, the specific heat is mainly vibrational, i.e. 2 degrees of freedom - one pe and one ke - for each direction of vibration (= 3 for an isotropic solid).

$\rightarrow U = 6 \times \frac{1}{2} N_0 k_B T$, per mole this is $U_m = 3RT$

$\therefore$ for a solid, the molar heat capacity $C_{V_m} = \left(\frac{\partial U_m}{\partial T}\right)_V = 3R$

Dulong-Petit Law

This is true for a very large range of solids at room temperature. However at lower temperatures this quickly falls off (see fig. 36). This was explained by Einstein (and then Debye) as being due to the 'freezing' of thermal vibration modes (*phonons*) in the solid.

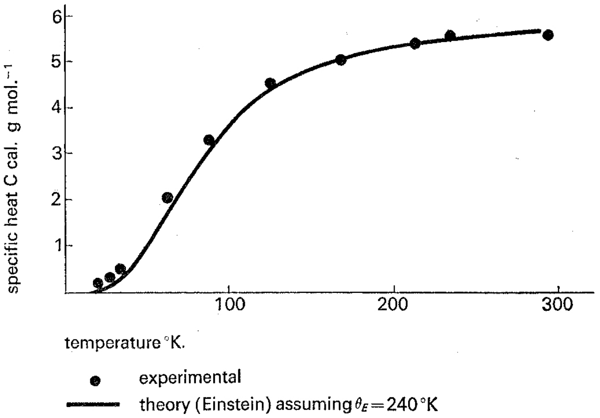

Figure 36: Variation of specific heat of solid with temperature

The fact that the specific heat capacity for all materials decreases at low temperatures has practical consequences. For example, it makes it much more difficult to cool a sample to a very low temperature. Cooling a sample depends upon putting a sample in contact with a 'sink' , that is, a large object that is already at a lower temperature so that there is a heat transfer, ΔQ, out of the sample into the sink, thus lowering the temperature of the sample and not increasing the temperature of the sink too much. At very low temperatures, the sink has a low heat capacity, so avoiding a T increase is very difficult to achieve.

9 Non-ideal gases

9.1 van der Waals Equation of State

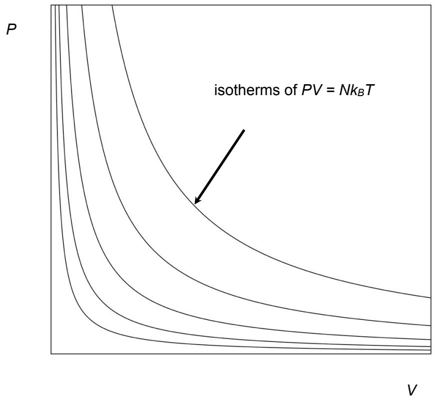

Figure 37: Isotherms for an ideal gas

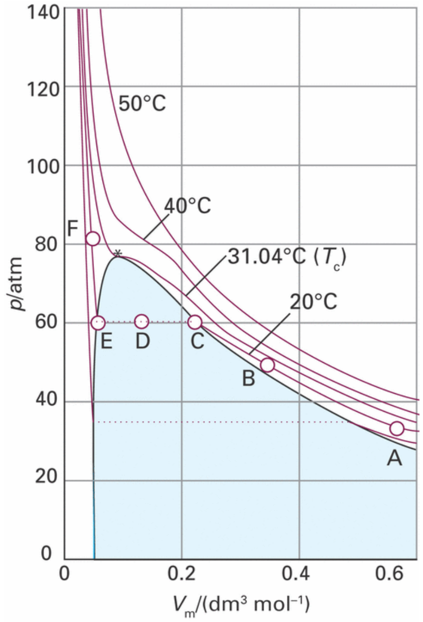

Figure 38: Isotherms for CO_2 (experimental data)

Experimental data shows that many gases behave far from ideal under certain conditions of P, T, and V. Consider the experimental isotherms of CO_2 (fig. 38 and its behaviour under compression. Near A, the gas behaves in accordance with Boyle's law; deviations appear when the volume is reduced to B.

At C (about 60 atm), the piston slides in without any further rise in pressure: this stage is represented by the horizontal line CDE. Also to the left of C a liquid appears, and there are two phases separated by a sharply defined surface. As the volume is decreased from C through D to E, the amount of liquid increases. There is no additional resistance to the piston because the gas can respond by *condensing*. The pressure corresponding to the line CDE, when both liquid and vapour are present in equilibrium, is called the **vapour pressure** of the liquid at the temperature of the experiment.

At E, the sample is entirely liquid → any further reduction of volume requires the exertion of considerable pressure, as is indicated by the sharply rising line to the left of E.

Thus, for a *van der Waals gas*, the ideal gas equation of state ($PV = Nk_BT$) must be modified when we consider:

(a) molecules are hard spheres (not point particles) of *effective* volume b

(b) there are attractive forces between gas particles that act over a finite range

(i) → volume available for motion $= \ V - bN$ (N = total no. of molecules) and so $P(V - bN) = Nk_BT$

To calculate the effective volume b, we note that the closest distance of two hard-sphere molecules of radius r and volume $V_m (= \frac{4}{3}\pi r^3)$, is $2r$, so the volume excluded (per molecule) is $\frac{1}{2} \times \frac{4}{3}\pi(2r)^3 = 4V_m$, so $b \approx 4V_m$ (the $\frac{1}{2}$ arises because a pair of molecules share this volume).

(ii) A molecule in the centre experiences attractive forces from all sides. These forces will cancel on average but will have an overall effect of reducing the no. of molecules hitting the wall. Pressure depends on both the *frequency of collisions* with the walls and the *force of each collision*. Both the frequency of the collisions and their force are reduced by attractive interactions, and they each act with a strength proportional to $n \ (= N/V)$. Therefore, the overall pressure is reduced in proportion to $(N/V)^2$.

$\therefore$ reduction in pressure, $\Delta P \propto n^2 \quad \rightarrow \quad \Delta P = -a(N/V)^2$ (a is proportionality constant)

Hence the ideal gas pressure is reduced by this amount, $P = P_{\{\text{ideal gas}\}} - \Delta P$

(where $P_{\{\text{ideal gas}\}}$ includes the above volume correction.)

$\rightarrow \quad P = Nk_BT/(V - bN) - a(N/V)^2$

OR

$$\boxed{(P + a(N^2/V^2))(V - Nb) = Nk_BT} \tag{16}$$

van der Waals equation of state

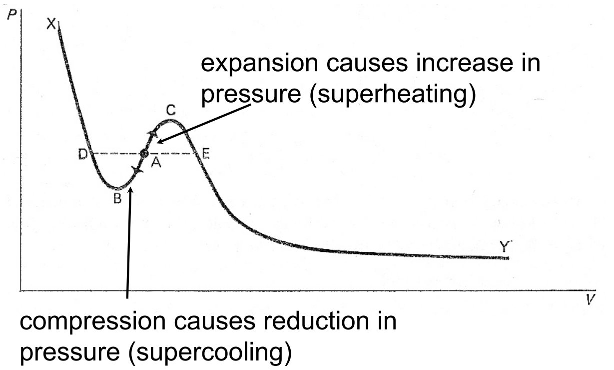

Figure 39: typical van der Waals isotherm

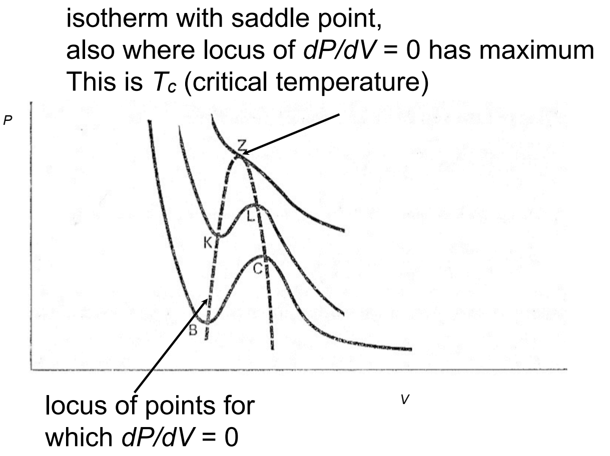

Figure 40: Isotherms for $T < T_c$

The constants a and b in eqn. 16 are called the **van der Waals coefficients**. They are characteristic of each gas but independent of temperature. At low T van der Waals isotherms oscillate and have max and min (figs. 39 & 40). Between two points where PV = constant, phases can be mixed. Above a *critical temperature* T_c, this mixed phase region does not exist, and so there is no clear boundary between gas and liquid phases.

Gases at $T > T_c$ and high pressure are called *supercritical fluids* having liquid like densities but expand (like a gas) to fill the volume.

9.2 *Internal Energy*

Let us revisit the internal energy of a system containing monatomic gas particles, and this time we shall assume a simplified potential in which $-\epsilon$ is constant over a volume such that if a 2nd molecule lies within this certain interaction volume V_{int}, $U = -\epsilon$, but if the 2nd molecule is outside V_{int}, then $U = 0$ (fig. 41 & 42).

→ no. of molecules in $V_{int} = nV_{int} = NV_{int}/V$

and the total no. of such interactions are; $= \frac{1}{2}N(NV_{int}/V)$ [Nb. $\frac{1}{2}$ so as to not count same interaction twice]

Thus the total p.e. between particles $= -(1/2)\epsilon(N^2/V)V_{int}$

$$U = \frac{3}{2}Nk_BT - aN^2/V \tag{17}$$

Internal energy for monatomic real gas

where $a = \frac{1}{2}\epsilon V_{int}$.

Equation 17 successfully accounts for the potential that exists between gases that are subject to van der Walls forces (i.e. a van der Waal gas). It is a more accurate description of the internal energy for most real gases and provides the key to explaining phenomena such as free expansion.

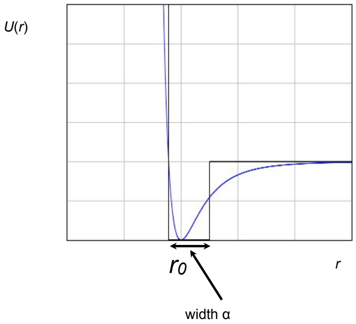

Figure 41: simplified van der Waals force

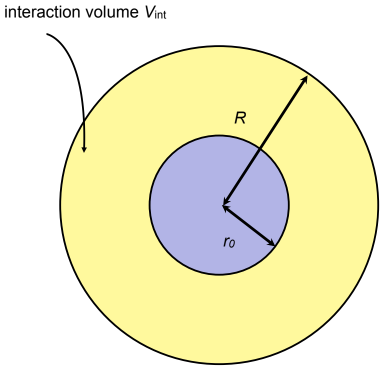

Figure 42: volume of potential

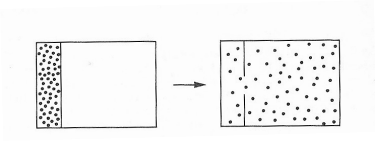

Figure 43: 2 compartments gas and vacuum separated by partition - chamber is thermally insulated

9.3 *Free expansion*

Consider an isolated system comprising of a gas that is placed inside one part of a partitioned container (fig. 43). We can assume the empty compartment is under vacuum. Naturally, if the partition is removed the gas will expand and fill the volume. We note that no work has been done [i.e. no pressure-induced piston movement] and by considering the first law, ΔU must necessarily be equal to zero.

For an ideal gas: $\frac{3}{2}Nk_BT$ = const. → T = const [since a volume increase is accompanied by a pressure decrease]. With a van der Waals gas we find however that:

$\frac{3}{2}Nk_BT - aN^2/V =$ const.

The experiment dictates that the overall volume increases → aN^2/V decreases → $\frac{3}{2}Nk_BT$ must decrease accordingly [so that the difference remains constant]. This implies that T also decreases - i.e. the gas cools upon expansion which is indeed the case. If we consider a micro picture, as the gas expands the molecules move further apart on average → the intermolecular potential increases whilst ke decreases. This forms the basis of **liquification** of air (Joule-Thomson process). At room temperature, all gases except hydrogen, helium and neon cool upon expansion by the Joule-Thomson process. The important point to note is that ideal gas behaviour does not predict this effect which is prevalent in real gases.

10 Phase Changes

A phase is a form of matter that is uniform throughout in chemical composition and physical state. A *phase change* is the conversion from one phase into another phase and occurs at a characteristic temperature for a given pressure. Phase changes usually indicate a *change in internal order* of the particles that make up the bulk matter. One of the most succinct ways of presenting the physical changes of state that a substance can undergo is in terms of its **phase diagram**.

10.1 PVT surface for ideal gas

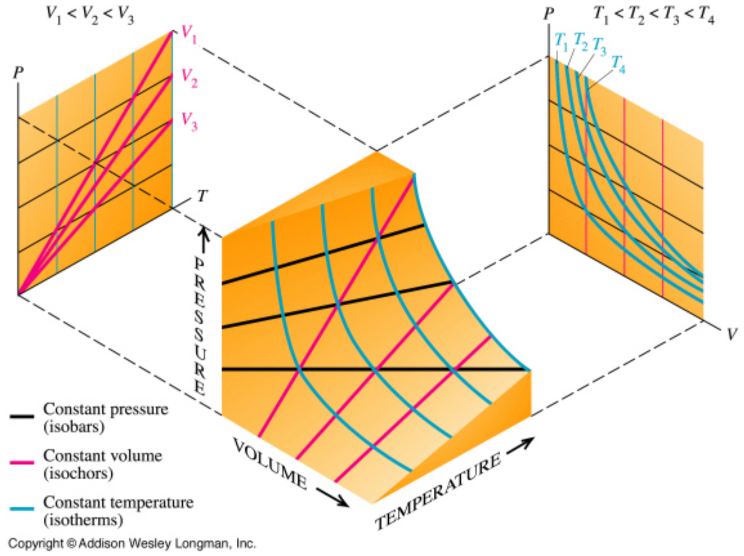

Figure 44: Quasistatic processes follow a path on the PVT surface. Usually plot projection in PV or PT

A phase diagram of a pure substance shows the regions of pressure and temperature at which various phases are thermodynamically stable (fig. 45 & 46). In fact, any two intensive variables could be used but in this section, we will mainly concentrate on pressure and temperature. The lines separating the regions are known as **phase boundaries** (or *coexistence curves*) and show the values of P and T for which two phases coexist in equilibrium.

If we start with the a (simplified) gas that obeys the ideal gas equation of state: $P = Nk_BT/V$, and consider the corresponding sets of isotherms, isochores, and isobars, a PVT surface plot can be constructed (see fig. 47). Projections of the constant-temperature curves (fig. 46) and constant-pressure curves (fig. 45) on the PV-plane correspond to the curves shown in fig 47. Such a surface is a useful qualitative tool for understanding the behaviour of materials under various conditions of temperature and pressure.

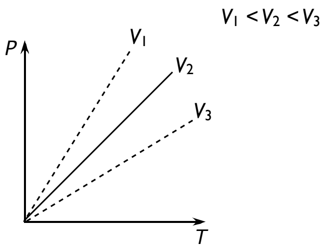

Figure 45: PT projection (isochor)

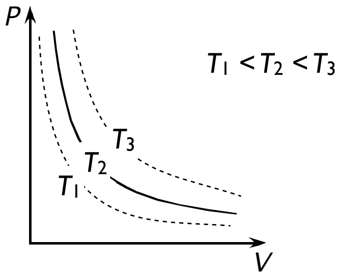

Figure 46: PV projection (isotherm)

10.2 *PVT surface for real substance*

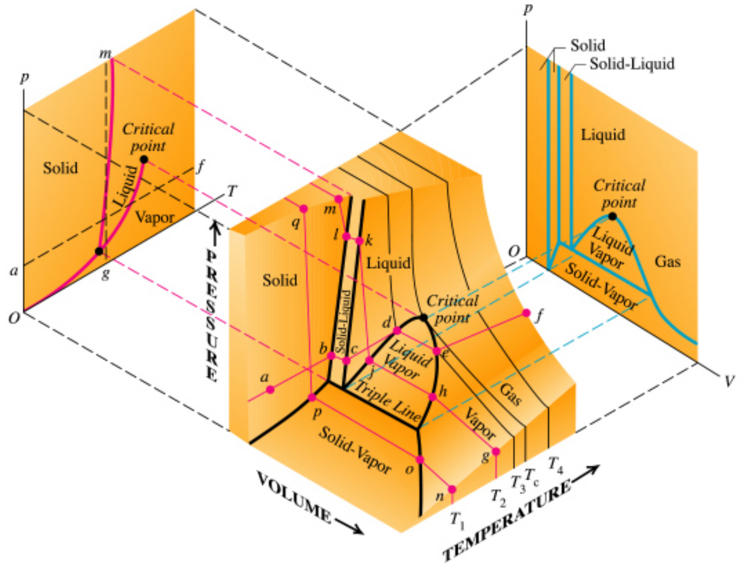

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Figure 47: PVT surface for real substance

For an ideal gas, *inter-particle interactions* - responsible for the formation of liquids and solids - are neglected. However, when one examines the behaviour of a real gas experimentally, there are regions on the PVT surface where the gas behaves far from ideal.

Isobaric changes:
a→b: solid T rises
b: starts to melt
b→c: solid / liquid co-exist, T constant
c→d: liquid, T rises
d: starts to vapourise
d→e: liquid / gas coexist, T constant
e→f: gas, T rises

All three phases exist at a unique *triple point* TP. The liquid-gas boundary ends at the *critical point* CP. Liquids can only exist below the *critical temperature* T_c.

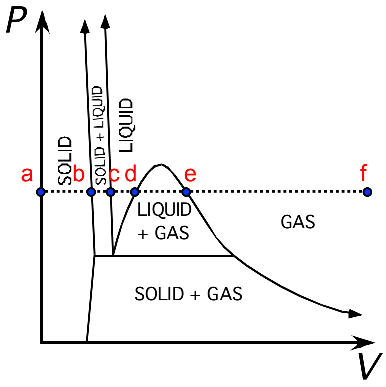

Figure 48: PV plot for real substance

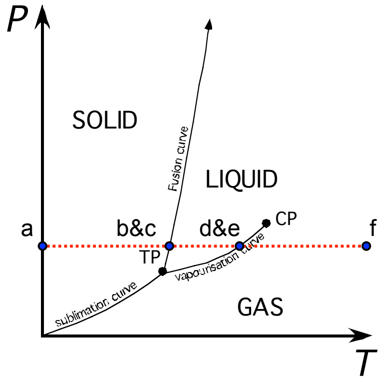

Figure 49: PT plot for real substance

10.3 *Isotherms of real substances*

$T_1 < T_{TP}$: gas condenses into solid

$T_{TP} < T_2 < T_c$: gas condenses into liquid, then liquid freezes into solid

$T_3 > T_c$: gas just gets denser, eventually condenses into solid [supercritical fluid]

Solids & liquids are hard to compress, that is, a large ΔP implies a small $\Delta V \rightarrow$ isotherms are very steep in solid & liquid regions (also different solid phases can exists e.g. graphite and diamond).

When the phase diagram for water is examined (fig. 52), The ice/water boundary has a very steep *negative slope* (from left to right), which means that the melting temperature *falls* with increasing pressure. The reason for this quite unique behaviour can be traced to the fact that there is a decrease in volume upon melting; it is more favourable for the solid to transform to a liquid as the pressure is raised. This is due to the very open structure of ice crystals as the *hydrogen bonds* that hold the molecules together also keep them apart. As the structure is heated, there is a partial collapse of the (hydrogen-bonded) structure and the resulting liquid becomes more dense than the solid. For this reason, water is most dense at $\approx 4^0$ C.

The solid phases of ice differ in the arrangement of water molecules: under the influences of high pressures, hydrogen bonds buckle and the H_2O molecules adopt different arrangements (conformations) called **polymorphs**. Such polymorphism may contribute to the advance of glaciers since ice at the bottom of a glacier is under tremendous pressures where it rests on jagged rocks.

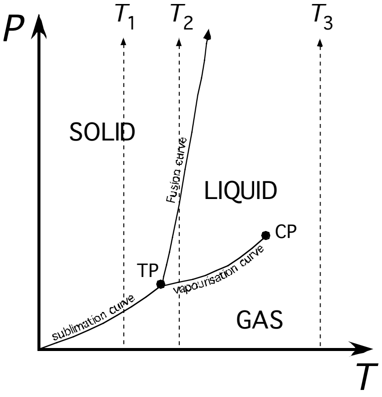

Figure 50: Isotherms on PT plot

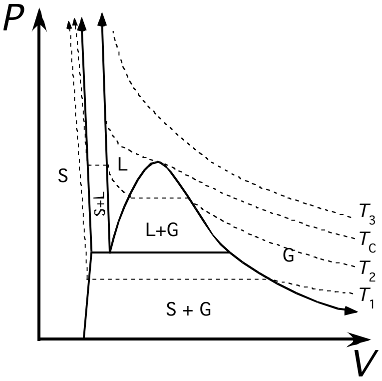

Figure 51: Isotherms on PV plot

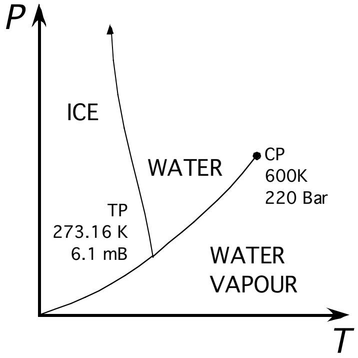

Figure 52: PT projection for H_2o, showing that unusually water contracts on melting.

10.4 *Latent Heats*

The change between phases is not instantaneous. A region exists in the PT diagram where phases can coexist, whilst heat is entering or leaving the system at the same temperature.

Heat required to cause complete change between phases = latent heat.

Latent heat of *vaporisation* L_v = heat required to change a liquid to a gas

Latent heat of *fusion* L_f = heat required to change solid to liquid

Latent heat of *sublimation* L_s = heat required from solid to gas for $T < T_p$ or $T > T_c$

Bond strength, ϵ, related to L_s ($\approx L_f + L_v$ if melting and boiling points are close.)

$L_s = \frac{1}{2} N n_N \epsilon$

where N = number of molecules, n_N = number of nearest neighbours and the $\frac{1}{2}$ is because each bond is shared. Also $L_v >> L_f$ since melting requires breaking approximately one bond, as opposed to vaporisation which will require breaking bonds to all nearest neighbours.

Typically we find that the binding energy ϵ can give an approximate estimate for the boiling point of a substance,

$$\text{e.g. } \epsilon \quad = \frac{n_d}{2} k_B T_{boil} \rightarrow \quad T_{boil} = \frac{2}{n_d} \frac{\epsilon}{k_B}.$$

11 *Properties of fluids*

In reality, most matter exists in two states: **solid**, and **fluid**, with the fluid state being commonly divided into *gases* and *liquids*. Solids differ from liquids and liquids from gases in terms of the spacing and latitude of motion of their molecules, these variables being large in gases, smaller in liquids and extremely small in solids. Such fundamental facts account for a huge array of physical properties like the familiar compactness and rigidity of form possessed by solids, the ability of liquid molecules to move freely within a liquid mass, and the ability of gases to fill completely any container in which it is placed; whilst a liquid has a definite volume and defined surface. In spite of the mobility and spacing differences, fluids can be considered as *continuous* with no voids or holes and we find that this assumption proves entirely satisfactory for most science and engineering problems.

Fluids are things which *flow*, gases are compressible, whilst liquids can be considered $\sim$ incompressible. You might feel a little uneasy treating liquids and gases by the same principles considering their obvious differences of compressibility. Usually when compressibility is of small importance then most fluid problems can be solved using the principles of mechanics; when compressibility dominates, thermodynamics and heat transfer concepts must also be incorporated. In this lecture we will investigate fluids from two different perspectives; namely **hydrostatics** (i.e. fluids at rest), and **hydrodynamics** (fluids in motion).

11.1 *Hydrostatics - Buoyancy*

In section 5.1, we derived the hydrostatic equation by considering an isothermal atmosphere; it was found that pressure *decreases* exponentially with *height*, z. When considering liquids such as water, P *increases* with *depth* in water, h, due to the weight of water above.

for an isothermal atmosphere (from eqn. 6) $\frac{\mathrm{d}P}{\mathrm{d}z} = -\rho g$

z = height above surface, ρ = density of air

for water,

$$\boxed{\frac{\mathrm{d}P}{\mathrm{d}h} = \rho g}$$

h = depth below surface (= $-z$), ρ = density of water

water is incompressible i.e. ρ = const. Thus by separating the variables and solving we obtain:

$\rightarrow$ $\boxed{P = P_0 + \rho g h}$ (P_0 is P at surface)

Often, the above equation may be interpreted as:

$P_{absolute} = P_{atmospheric} + P_{gauge}$
and in most everyday circumstances (e.g. determining pressure below sea level, or the pressure in a car tyre), it is the *gauge pressure* (pressure relative to atmospheric pressure) that is of interest.

The pressure at any two points in a fluid at the same depth will be equal - regardless of the shape of the container - and this leads directly to **Pascal's law** which states that:

pressure applied to an enclosed fluid is transmitted undiminished to all parts of the fluid and the walls of the containing vessel (Pascal's Law)

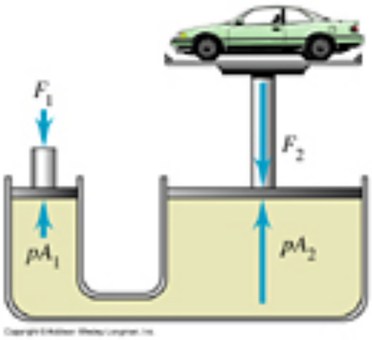

Figure 53: Hydraulic lift: application of Pascal's law.

This law forms the basis of hydraulic lifts where a piston of small cross-sectional area, A_1 exerts a force F_1, on the surface of a liquid (see fig. 53). The applied pressure, p, is transmitted to all parts of the fluid and so acts as a 'force-multiplying' device (where $F_2 \propto A_2/A_1$). Hydraulic breaks, barber & dentist chairs, and many elevators all operate under this principle.

Now consider an immersed object of area A (as in fig. 54). If the object is less dense than the liquid it will float and vice-versa. We shall assume the object is in mechanical equilibrium.

Total force $F_B = -\{P_0 + \rho gh\}A + \{P_0 + \rho g(h+l)\}A - mg = \rho g l A - mg$ where lA = volume

$\therefore$ effective weight of the object is reduced by $\rho g l A = \rho g V_{disp}$ = weight of water displaced = **buoyancy**.

Archimedes' principle states that:

a fluid exerts an upward force on a submerged object that is equal to the weight of liquid displaced by the object (Archimedes' Principle)

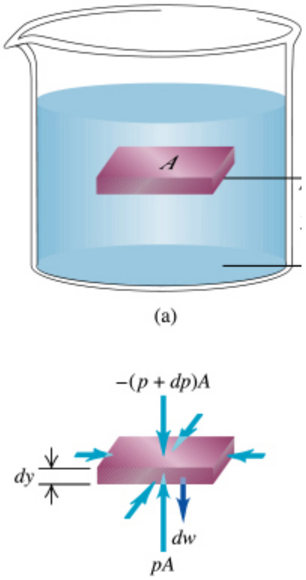

Figure 54: submerged cube

A practical application of Archimedes' principle can be found in a *hydrometer* used to measure liquid densities. Briefly, the buoyancy of a calibrated float is submerged into a liquid until the weight of the fluid it displaces exactly equals it's own weight. The hydrometer will float higher in more dense liquids than less dense ones, and the densities can be read off a calibrated scale in the stem at the top of the device.

11.2 *Surface tension*

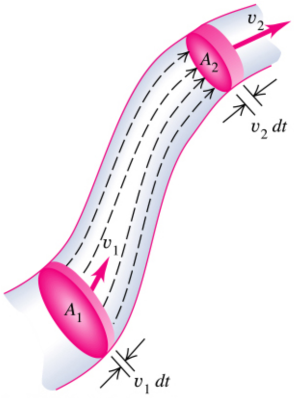

Figure 55: constriction in a pipe

In discussing the liquid phase during lecture 10, the effect of the boundary surface on the properties of the liquid had been neglected. Liquids try to minimize their surface area. In the absence of a gravitational field, a liquid drop will assume a spherical shape (as opposed to a teardrop shape), as this ensures that the maximum number of molecules is surrounded by neighbouring molecules. The interaction between molecules in a liquid is attractive , therefore minimizing the surface-to-volume ratio will minimize the energy. A liquid surface is like a stretched elastic membrane, and the force responsible for this is *surface tension*, γ (units Nm^{-1}). Its magnitude will decrease with increasing temperature due to the intermolecular forces becoming relatively weaker.

Surface tension is important for small liquid drop sizes (say millimeter-sized), for large quantities of liquid though, the ratio of surface area to volume is quite small, rendering surface tension small compared to pressure forces. Surface tension plays a critical role in bubble formation and it can be shown that the work done in creating additional surface area

$dW = \gamma dA$,

where dA is the element of unit of area (PS4). Capillary rise and capillary depression are caused by pressure differences across a curved surface and this is due to surface tension.

11.3 Hydrodynamics - continuity equation

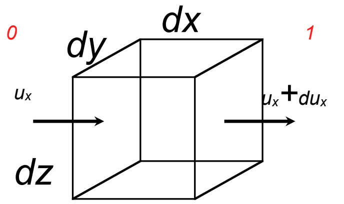

Figure 56: flux through infinitesimal vol.

Let R = mass flow rate = mass of fluid flowing through given area per unit time

e.g. pipe area A, flow speed u, mass of fluid past this point in $\Delta t = \rho u \Delta t A$

$$R = \rho u A \tag{18}$$

Consider a steady flow within a pipe of variable area. Fluid is not created or destroyed [i.e. matter conserved], so

$$\rho_1 u_1 A_1 = \rho_2 u_2 A_2 \tag{19}$$

Continuity equation (steady flow)

For an incompressible liquid $\rho_1 = \rho_2$, so

$\rightarrow \quad \boxed{u_1 A_1 = u_2 A_2}$

In other words *things exit smaller nozzles faster*, this is the principle behind how a perfume atomiser or a shower head works. In reality, every point in fluid has some flow velocity, i.e. u in fluid is a vector field

$\mathbf{u} \cdot \mathbf{A}$ = flux = volume of fluid through area per unit time

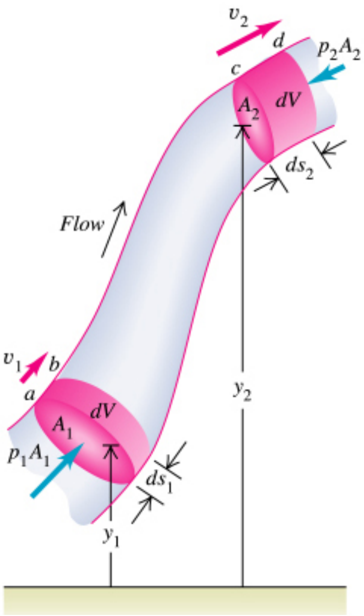

Figure 57: Energy balance for a flow

Consider the flux through an infinitesimal volume $(\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z)$ due to a flow velocity $\mathbf{u}$. The change of mass of the element is thus equal to the difference in *mass flux* between the two sides, i.e.

$\Delta\rho\,(\mathrm{d}x\,\mathrm{d}y\,\mathrm{d}z) = \{(\rho_0 u_{x0}\,\mathrm{d}y\,\mathrm{d}z) - (\rho_1 u_{x1}\,\mathrm{d}y\,\mathrm{d}z)\}\Delta t$

$\rightarrow \quad \dfrac{\Delta\rho}{\Delta t} = -\Delta(\rho u_x)/\mathrm{d}x \quad$ taking the limit $\quad \rightarrow \quad \dfrac{\partial\rho}{\partial t} = -\dfrac{\partial(\rho u_x)}{\partial x}$

Generalising $\mathbf{u}$ to be in any direction,

$$\frac{\partial\rho}{\partial t} + \nabla\cdot(\rho\mathbf{u}) = 0 \tag{20}$$

Continuity equation (differential)

11.4 *Fluid flows in ideal fluid*

An ideal fluid is one without viscosity. For a flow at a height h, area A, velocity u and pressure P,

Volume of liquid flowing past point 1 in time $\mathrm{d}t = u_1 \mathrm{d}t\, A_1$,
so work done by pressure of gas $w_a = u_1 \mathrm{d}t\, A_1 P_1$,
mass of this liquid = density * volume = $\rho \times u_1 \mathrm{d}t\, A_1$,
the kinetic energy it carries is $w_b = \frac{1}{2}\rho\, u_1 \mathrm{d}t\, A_1 \times u_1^2$,
and its potential energy $w_c = \rho\, u_1 \mathrm{d}t\, A_1 \times g h_1$
Since energy is conserved $(w_a + w_b + w_c)_1 = (w_a + w_b + w_c)_2$
$(u_1 \mathrm{d}t\, A_1 P_1) + (\frac{1}{2}\rho\, u_1 \mathrm{d}t\, A_1 u_1^2) + (\rho\, u_1 \mathrm{d}t\, A_1\, g h_1) = (u_2 \mathrm{d}t\, A_2 P_2) + (\frac{1}{2}\rho\, u_2 \mathrm{d}t\, A_2 u_2^2) + (\rho\, u_2 \mathrm{d}t\, A_2\, g h_2)$
but for an incompressible fluid $u_1 A_1 = u_2 A_2$, so

$$\boxed{P_1 + \frac{1}{2}\rho u_1^2 + \rho h_1 g = P_2 + \frac{1}{2}\rho u_2^2 + \rho h_2 g} \tag{21}$$

Bernouilli's Equation

Bernouilli's equation says that increasing velocity flows must have a corresponding decrease in pressure. This is the basis of flight in aerofoils and curled free-kicks.

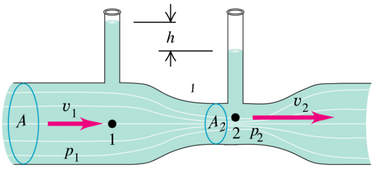

Figure 58: A Venturi meter used to measure flow speeds [see Section 14.5 - Young and Freedman]

11.5 *Fluid equation of motion: acceleration produced by force*

Equation of motion for a fluid element: $(\Delta p = F\Delta t)$

$$\Delta p = \Delta(\rho\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z\, u_x) = \{(P_0\, \mathrm{d}y\, \mathrm{d}z) - (P_1\, \mathrm{d}y\, \mathrm{d}z)\}\Delta t$$

$$\Delta(\rho\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z\, u_x) = \{(P_0\, \mathrm{d}y\, \mathrm{d}z) - (P_1\, \mathrm{d}y\, \mathrm{d}z)\}\Delta t$$

$$\rho\frac{\Delta u_x}{\Delta t} = -\frac{\Delta P}{\mathrm{d}x} \quad \text{taking the limit} \quad \rightarrow \quad \rho\frac{\mathrm{d}u_x}{\mathrm{d}t} = -\frac{\mathrm{d}P}{\mathrm{d}x}$$

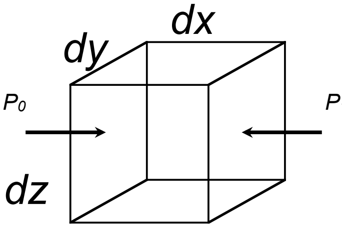

Figure 59: momentum conservation in an infinitesimal fluid element

One complication is that the exact derivative is only true for the equation of motion of all the fluid particles. For a fluid element, one must consider the change in the momentum in the box, not just from the action of the force but also due to particles flowing in and out of the box. In other words, the total derivative is not just a function of time, but also of space as well, i.e.,

$$\rho\left(\frac{\mathrm{d}}{\mathrm{d}t}\right)u_x = \rho\left(\frac{\partial}{\partial t} + \frac{\partial x}{\partial t}\frac{\partial}{\partial x}\right)u_x = \rho\left(\frac{\partial}{\partial t} + u_x\frac{\partial}{\partial x}\right)u_x$$

The term in the bracket is called the convective derivative.

Generalising to three dimensions and including a friction term too (i.e. the viscosity), the equation of motion on a fluid element is,

$$\boxed{\rho\left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u}\cdot\nabla\mathbf{u}\right) = -\nabla P + \eta\nabla^2 u} \tag{22}$$

Navier-Stokes equation

This is a non-linear PDE and difficult to solve.

The last (vicosity) term allows fluids to move together in laminar flow. The ratio of intertial forces / viscous terms, is called the

Reynold's number.

$$R_e = \frac{\rho v^2/L}{\eta v/L^2} = \frac{\rho v L}{\eta}$$

For $R_e \gg 1$ (usually above 2000) viscosity cannot pull a fluid together and the flow becomes turbulent.